

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



EP0247203

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : C08G 69/26, C08L 77/00, 67/02 B32B 27/34	A2	(11) International Publication Number: WO 87/02680 (43) International Publication Date: 7 May 1987 (07.05.87)
(21) International Application Number: PCT/JP86/00542		Kanagawa 229 (JP).
(22) International Filing Date: 28 October 1986 (28.10.86)		(74) Agent: MAYEDA, Sumihiro; Patent Department, Teijin Limited, 1-1, Uchisaiwaicho 2-chome, Chiyoda-ku, Tokyo 100 (JP).
(31) Priority Application Numbers: 60/244110 60/244111		(81) Designated States: CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), KR, NL (European patent), US.
(32) Priority Dates: 1 November 1985 (01.11.85) 1 November 1985 (01.11.85)		
(33) Priority Country: JP		Published <i>Without international search report and to be republished upon receipt of that report.</i>
(71) Applicant (for all designated States except US): TEIJIN LIMITED [JP/JP]; 11, Minamihonmachi 1-chome, Higashi-ku, Osaka-shi, Osaka 541 (JP).		
(72) Inventors; and (75) Inventors/Applicants (for US only) : YAMASHIRO, Seiichi [JP/JP]; 2-11, Hanakoganei Minami-machi 3-chome, Kodaira-shi, Tokyo 184 (JP). MATSUBAYASHI, Tooru [JP/JP]; 17-7, Yookoodai 3-chome, Sagamihara-shi, Kanagawa 229 (JP). SAKAI, Kouichi [JP/JP]; 3-6, Motohashimoto-cho, Sagamihara-shi, Kanagawa 229 (JP). TOYAO, Hiroshi [JP/JP]; 9-19, Seishin 7-chome, Sagamihara-shi,		

(54) Title: POLYAMIDE PACKAGING MATERIAL

(57) Abstract

A polyamide packaging material comprises a copolymerized polyamide comprising 10 to 90 mole% of tetramethylene adipamide units and 90 to 10 mole% of tetramethylene isophthalamide units. The copolymerized polyamide has excellent gas barrier properties and good moldability.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria
AU Australia
BB Barbados
BE Belgium
BG Bulgaria
BJ Benin
BR Brazil
CF Central African Republic
CG Congo
CH Switzerland
CM Cameroon
DE Germany, Federal Republic of
DK Denmark
FI Finland

FR France
GA Gabon
GB United Kingdom
HU Hungary
IT Italy
JP Japan
KP Democratic People's Republic of Korea
KR Republic of Korea
LI Liechtenstein
LK Sri Lanka
LU Luxembourg
MC Monaco
MG Madagascar

ML Mali
MR Mauritania
MW Malawi
NL Netherlands
NO Norway
RO Romania
SD Sudan
SE Sweden
SN Senegal
SU Soviet Union
TD Chad
TG Togo
US United States of America

- 1 -

SPECIFICATION

Title of the Invention

Polyamide Packaging Material

Technical Field

5 The present invention relates to a packaging material made of a polyamide, more particularly, it relates to a packaging material made of a copolymerized polyamide having excellent gas barrier properties, strength and heat resistance.

Background Art

A material having high gas barrier properties is required in packaging, especially in food packaging to elongate the shelf life of the food or to keep the freshness of the food.

15 For example, in the case of packaging a food containing an oleaginous component, a packaging material having excellent oxygen barrier property is desired to prevent the progress of the deterioration of the food caused by the transmission of oxygen.

20 Furthermore, a packaging material having excellent barrier property to carbon dioxide gas is desired for the container of a carbonated beverage, etc. to keep its freshness. Various materials have been developed to meet the above requirements, for example, polyvinylidene chloride, ethylene-vinyl alcohol copolymer, polyamide, polyethylene 25 terephthalate, etc., and various methods have been proposed.

For example, there have been proposed a method in which a polymer film is coated or laminated with a gas barrier material such as polyvinylidene chloride or a saponified

- 2 -

ethylene/vinyl acetate copolymer (vide; Japanese Unexamined Patent Publications No. 117565/79 and No. 64839/81), and a method in which a polyester is blended with a gas barrier material (European Unexamined Patent 105826). To satisfy 5 various requirements other than gas barrier properties such as mechanical strength, moisture permeability, weathering resistance, etc., an article composed of two or more polymers is formed or converted to a multi-layer structure by co-extrusion or co-injection technique.

10 Among the above-mentioned materials, polyamide has excellent processability, heat resistance and strength, and is used widely as a packaging material; however, the gas barrier properties of nylon 6 and nylon 66 are not necessarily sufficient, and the development of a new material having 15 further excellent gas barrier properties is wanted.

5

10

15

20

25

Disclosure of Invention

It is a primary object of the present invention to provide a polyamide packaging material which is excellent moldability and gas barrier properties. A further object of 20 the present invention is to provide a packaging material suitable for a multi-layer structure composed of the polyamide component and polyethylene terephthalate component.

This invention is directed to a polyamide packaging material excellent in the resistance to the permeation 25 of oxygen and carbon oxide gases, which comprises a copolymerized polyamide comprising tetramethylene adipamide unit and tetramethylene isophthalamide unit.

Best Mode of Carrying out the Invention

- 3 -

Copolymerized polyamide valuably used for the packaging material of the present invention comprises 10 to 90 mole% of tetramethylene adipamide units and 90 to 10 mole% of tetramethylene isophthalamide units. It has been unexpectedly found that by copolymerizing polytetramethylene adipamide with the isophthalic acid, the gas barrier property is highly improved as well as moldability.

The ratio of tetramethylene adipamide unit and tetramethylene isophthalamide unit is preferably 20:80 to 80:20.

10 In a case of manufacturing a multi-layer structure comprising a polyethylene terephthalate layer and a polyamide layer, the copolymerized polyamide layer having a tetramethylene adipamide content of not more than 90 has a rate of crystallization suitable for the drawing or stretching of said multi-layer structure. In other words, when the ratio of tetramethylene adipamide unit exceeds 90, the rate of crystallization of the polymer becomes extremely high, and the clouding phenomenon tends to occur in the obtained molded article such as preform. On the other hand, when the ratio of tetramethylene isophthalamide content exceeds 90, the preform comprising the multi-layer structure above-mentioned must be preheated at the vicinity of 150°C in the drawing step, therefore, the clouding or crystallization of polyethylene terephthalate layer cannot be avoided.

25 The copolymerized polyamide may comprises other comonomer component, so far as the characteristic properties are not degraded. Accordingly, the polyamide of the present invention contains other comonomer units in an amount of less than 20%

- 4 -

of the whole recurring units, and a part of the tetra-methylenediamine and a part of adipic acid or isophthalic acid are substituted with one or more kinds of other diamines, aminocarboxylic acids, lactam or dicarboxylic acids. For example, the comonomer components are aliphatic diamines such as ethylenediamide, trimethylenediamine, hexamethylenediamine, etc.; aromatic diamines such as phenylenediamine, xylidine, 3,6-diaminoacridine, N-methyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, tolylenediamine, etc.; aliphatic cyclic diamines such as 1,2-diaminocyclobutane, etc.; aliphatic aminocarboxylic acids such as glycine, alanine, valine, etc.; aromatic aminocarboxylic acids such as phenylalanine, amino-benzoic acid, etc.; alicyclic aminocarboxylic acids such as aminocyclohexanecarboxylic acid, etc.; lactam such as β -propiolactam, γ -butyrolactam, δ -caprolactam, etc.; aromatic dicarboxylic acids such as terephthalic acid, naphthalene-dicarboxylic acid, diphenyldicarboxylic acid, diphenoxo-ethanedicarboxylic acid, diphenyl ether dicarboxylic acid, diphenyl sulfone dicarboxylic acid, diphenyl ketone dicarboxylic acid, sodium-sulfoisophthalic acid, dibromoterephthalic acid, etc.; alicyclic dicarboxylic acids such as decalinedicarboxylic acid, etc.; and aliphatic dicarboxylic acids such as succinic acid, sebacic acid, etc.

The relative viscosity (η_{rel} ; 1.0 wt% solution using 96% sulfuric acid as the solvent; measured at 20°C) of the polyamide of the present invention is preferably 2.0 or higher from the viewpoint of the strength of the obtained film or article.

- 5 -

The copolymerized polyamide can be produced by the conventional method known as the process for the production of polyamide. For example, it can be produced by condensing tetramethylenediamine with isophthalic acid, and 5 tetramethylenediamine with adipic acid to form respective salts, and subjecting the resultant reaction product to the polycondensation reaction. Various polycondensation catalysts, stabilizers, etc. can be used in the above production process. If necessary, other additives such as 10 colorants fluorescent brighteners, oxidation stabilizers, ultraviolet absorbing agents, antistatic agents, flame-retardants, etc. may be used in the process.

The polyamide packaging material of the present invention is, for example, a film and a container such as bottle, cup, 15 etc. produced by a molding method accompanying with the drawing process.

The film or the sheet can be manufactured by the conventional methods known as the film-forming or sheet-forming methods. For example, the resin is dried at a 20 temperature not lower than 80°C for 30 minutes or more, melted and extruded with an extruder furnished with a T-die or I-die, etc., and quenched to obtain an undrawn film or sheet, which may be further drawn along uniaxial or biaxial directions to obtain a drawn film or sheet.

25 Furthermore, the polyamide packaging material of the present invention is used for one component of a multi-layer structure. The multi-layer structure comprises a layer of self-supportable polymer component, such as polyethylene

- 6 -

terephthalate, and a layer of the copolymerized polyamide component. A double-layer structure wherein the inner layer is a polyethylene terephthalate layer and the outer layer is a copolymerized polyamide layer, a triple-layer structure 5 wherein the inner and the outer layers are polyethylene terephthalate layers and the intermediate layer is made of the copolymerized polyamide, and the five-layer structure corresponding to the above triple-layer structure containing two adhesive interlayers inserted between the above three 10 layers are preferable. The weight ratio of the copolymerized polyamide layer is preferably 5 to 50 wt%, especially 10 to 30 wt% to keep the physical properties and to attain high gas barrier properties of the obtained multi-layer drawn polyester sheet or bottle.

15 Any combination of two or more polymers including the copolymerized polyamide may have an integral structure of a polymer-blend. The integral structure has also excellent gas barrier properties.

20 The polyethylene terephthalate that can be used in combination with the polyamide packaging material of the present invention is a polyester comprising at least 80 mole% of ethylene terephthalate units based on the total recurring units. A part of the terephthalic acid component may be replaced by at least one member selected from bifunctional 25 carboxylic acids; for example; aromatic dicarboxylic acids such as isophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acid, diphenoxymethanedicarboxylic acid, diphenyl etherdicarboxylic acid, diphenylsulfonedicarboxylic

- 7 -

acid; alicyclic carboxylic acids such as hexahydroterephthalic acid and hexahydroisophthalic acid; aliphatic dicarboxylic acids such as adipic acid, sebacic acid, and azelaic acid; and hydroxyacids such as p- β -hydroxyethoxybenzoic acid, p-hydroxybenzoic acid, and ϵ -hydroxycaproic acid, and/or a part of the ethylene glycol component may be replaced by at least one member selected from other glycols such as trimethylene glycol, tetramethylene glycol, hexamethylene glycol, decamethylene glycol, neopentyl glycol, diethylene glycol, 1,1-cyclohexane dimethyol, 1,4-cyclohexane dimethyol, 2,2-bis(4- β -hydroxyethoxyphenyl)propane, and bis(4- β -hydroxyethoxyphenyl)sulfone, and these copolyesters may be used as the polyethylene terephthalate so long as the above-mentioned requirement of the content of ethylene terephthalate units is satisfied. In view of the mechanical properties, preferably the inherent viscosity $[\eta]$ of the polyethylene terephthalate is at least 0.5, especially at least 0.6, as measured in o-chlorophenol as the solvent at 35°C.

As the packaging material of the present invention, there can be mentioned a container formed by the molding method including the drawing steps, such as a cup or bottle. Furthermore, the material may be a container obtained by the deep drawing of undrawn laminated sheet or a container obtained by drawing a bottom-closed laminated pipe. Moreover, a tray manufactured by the vacuum forming or the air pressure forming of a sheet is one of embodiments of the present invention.

The multi-layer drawn bottle of the present invention is

- 8 -

manufactured basically by the hitherto developed process for the forming of polyester bottles, that is, by the process comprising the forming of a multi-layer preform and the orientation blow-molding of the preform. The multi-layer preform can be formed e.g. by forming a multi-layer pipe composed of a polyethylene terephthalate layer and a copolymerized polyamide layer by the multi-layer co-extrusion technique, cutting the pipe to a prescribed length, and forming both ends in the desired forms of mouth and bottom by thermal forming.

As an alternative method, a preform having multi-layer structure can be manufactured by the multi-layer injection molding process wherein the copolymerized polyamide is injected successively to the inner surface, outer surface or between the layers of polyethylene terephthalate. The draw ratio of the bottle at the barrel portion in the drawing of the blow expansion of the multi-layer preform is preferably 1.2 or more, especially 2 or more in terms of areal ratio.

The packaging material of the present invention made of a polyamide has excellent gas barrier properties. For example, the carbon dioxide gas permeability constant of the material is 1/5 to 1/10 of that of nylon 6 and accordingly the material is extremely useful for the packaging of a material to which high gas barrier properties are especially required.

Furthermore, gas barrier properties of nylon 6, nylon 66 and polytetramethylene adipamide become poor in the presence of water, whereas the copolymerized polyamide of the present invention retains sufficient resistance to gas permeation under high humidity environment.

- 9 -

Moreover, an advantage of the present invention is that a multi-layer structure having good processability is prepared by using the conventional methods and equipments.

The present invention will now be described in detail with reference to the following examples. The properties mentioned in the examples are measured according to the following methods.

(a) Relative viscosity (η_{rel}) of the polyamide

Measured at 20°C using 96% sulfuric acid at 1.0 wt% concentration.

(b) Intrinsic viscosity of the thermoplastic polyester

Measured at 35°C using o-chlorophenol as the solvent.

(c) Oxygen gas permeability constant (P_{O_2}) and carbon dioxide gas permeability constant (P_{CO_2})

The transmission rates of oxygen gas and carbon dioxide gas were measured at 30°C by a GPM-200-type gas permeability tester (product of Lyssy Co., Switzerland) using a mixture of O_2 and CO_2 at a volume ratio (O_2/CO_2) of 80/20.

Comparative Examples 1 through 3

A polytetramethylene adipamide (hereinafter referred to as nylon 46) having an η_{rel} of 3.5 was prepared from tetramethylenediamine and adipic acid according to the method disclosed in the specification of Japanese Patent Unexamined Publication No. 149430/81. The nylon 46 was dried by a vacuum drier at 100°C for 24 hours, and a single-layer film having a thickness of about 100 μm was manufactured by using a 30mm-diameter extruder at cylinder temperature of 300°C and a

- 10 -

casting roll temperature of about 20°C.

The obtained film had an opaque white appearance.

For comparison, films of nylon 6 ($[\eta] = 1.2$) and nylon 66 ($[\eta] = 1.3$) were manufactured by similar methods.

5 The results obtained by the measurement of the gas barrier properties of these films are shown in Table 1.

Table 1

	Material of film	$P_{O_2} \times 10^{12}$ (cc·cm/cm ² ·sec·cmHg)	$P_{CO_2} \times 10^{12}$ (cc·cm/cm ² ·sec·cmHg)
Comparative example 1	nylon 46	0.5	2.0
Comparative example 2	nylon 6	1.6	10.5
Comparative example 3	nylon 66	2.2	11.3

10 It can be seen from Table 1 that nylon 46 has excellent
15 gas barrier properties, however, nylon 46 is not formed into a
transparent film.

20 Examples 1 and 2, Comparative Examples 4 and 5

25 Polyamides were prepared by the polycondensation of tetramethylenediamine, adipic acid and isophthalic acid. The η_{rel} , appearances and gas barrier properties of the polyamides are shown in Table 2.

- 11 -

Table 2

	Acid component (Molar ratio)		η_{rel}	Appearance of film	
	Adipic acid	Isophthalic acid			
5	Comparative Example 4	92	8	2.3	Opaque white
10	Example 1	75	25	2.1	Transparent
15	Example 2	60	40	2.6	Transparent
20	Comparative Example 5	0	100	2.3	Transparent

Examples 3 through 5 and Comparative Examples 6 through 10

Polyethylene terephthalate (hereinafter abbreviated as PET) having an intrinsic viscosity of 0.74 was dried at 160°C for 5 hours with hot air. Separately, the copolymerized polyamide shown in the table 3 was dried at 100°C for 24 hours in vacuum. The polyethylene terephthalate and the polyamide were supplied to the cylinders A and B of the ASB-50EX-T-type one-stage multilayer biaxial orientation stretch blow-molding machine made by Nissei ASB Machine Co. Ltd., respectively, and were injected by the co-injection molding into a mold cooled with cooling water of 15°C while setting the temperature of the cylinder A at 260 to 280°C and that of the cylinder B (for intermediate layer) at 240 to 300°C. A preform having a

- 12 -

weight ratio of the intermediate layer of 20 wt% was manufactured by this process. The preform had a cylindrical form closed at one end and having an outer diameter of 25 to 26 mm, a thickness of 3.5 mm and a total length of 155 mm.

5 The preform was pre-heated at a temperature of 120 to 150°C, the preform was drawn axially in a bottle-shaped mold and expanded laterally with compressed air to form a bottle having an outer body diameter of 82 mm, a total height of 280 mm, a barrel portion thickness of 250 to 360 μm , and an inner 10 volume of 1040 - 1050 ml. The drawability (blow-moldability) of the preform in the above procedure and the gas barrier properties measured by using the test pieces prepared by cutting the barrel of the bottle are shown in the table 3.

15

20

25

- 13 -

Table 3

	Copolymerized polyamide			Blow moldability	Drawing uniformity	Gas permeation constant (P _{CO₂}) (x10 ⁻¹² cc. cm/cm ² . sec. cmHg)		
	Monomer components (mol-base)	1,4-Diamino-butane	Adipic acid	Isophthalic acid	Relative viscosity	Transparency		
Example 3	100	75	25		2.1	Opaque white	Good	7.4
Example 4	100	60	40		2.6	Transparent	Good	4.9
Example 5	100	40	60		2.4	Transparent	Good	2.3
Comparative example 6	100	100	0		3.5	Clouding *	Unable to draw	-
Comparative example 7	100	92	8		2.3	Clouding *	Unable to draw	-
Comparative example 8	100	8	92		2.3	Clouding **	Drawable at 150°C giving nonuniform thickness	-
Comparative example 9	100	0	100		2.3	Clouding **	Drawable at 150°C giving nonuniform thickness	-
Comparative example 10	PET homopolymer				Transparent	Good	20.5	

Remarks: * Clouding of the intermediate layer (polyamide)

** Clouding of the outer layer (PET)

- 14 -

In the preheating step the polyethylene terephthalate outer layer of the preform of Comparative Example 9 got clouding and the obtained bottle (drawn preform) gave non-uniform wall thickness after drawing the partially crystallized preform.

5 Examples 6 through 8

Preforms were manufactured by using the copolymerized polyamide used in the Example 4, by the method similar to the Example 4 except for the thickness relationship between the 10 polyamide layer and the PET layer, which was varied in a manner shown in the table 4, and the drawabilities and the gas barrier properties of the preforms were measured.

10 The results are shown in the table 4.

15 It can be seen also from the table 4 that the bottle of the present invention has excellent moldability and gas barrier properties.

Table 4

	Thickness of polyamide layer (wt%)	Transparency	Drawing uniformity	Gas permeation constant (P _{CO₂}) x10 ⁻¹² cc·cm/cm ² ·sec·cmHg
Example 6	10	transparent	good	7.5
Example 7	30	transparent	good	3.0
Example 8	50	transparent	good	2.3

- 15 -

CLAIMS

1. A polyamide packaging material excellent in the resistance to the permeation of gases, which comprises a copolymerized polyamide comprising 10 to 90 mole% of tetra-
5 methylene adipamide units and 90 to 10 mole% of tetramethylene isophthalamide units.
2. A packaging material comprises a component of poly-
ethylene terephthalate and a component of copolymerized poly-
amide comprising 10 to 90 mole% of tetramethylene adipamide
10 units and 90 to 10 mole% of tetramethylene isophthalamide
units.
3. A packaging material as set forth in claim 2, wherein the polyethylene terephthalate component and the copolymerized polyamide component are formed into a multi-layer structure.
- 15 4. A packaging material as set forth in claim 2, wherein the polyethylene terephthalate component and the copolymerized polyamide component are blended and formed into an integral structure.

20

25

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.